Applied Catalysis B: Environmental 247 (2019) 115–123

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Continuous flow disinfection of WWTP secondary effluents by solar photo-Fenton at neutral pH in raceway pond reactors at pilot plant scale

I. De la Obra Jiménez[a,b], B. Esteban García[a,b], G. Rivas Ibáñez[a,b], J.L. Casas López[a,b], J.A. Sánchez Pérez[a,b,*]

[a] Solar Energy Research Centre (CIESOL), Joint Centre University of Almería-CIEMAT, 04120 Almería, Spain
[b] Department of Chemical Engineering, University of Almería, 04120 Almería, Spain

ARTICLE INFO

Keywords:
Wastewater disinfection
Photo-Fenton
Raceway pond reactor
Continuous flow
Solar photocatalysis

ABSTRACT

The feasibility of low cost reactors such as raceway pond reactors (RPRs) for micropollutant removal as well as pathogen inactivation has recently been reported. This study presents, for the first time, the inactivation of Total Coliforms, *Escherichia coli* and *Enterococcus* sp. in WWTP secondary effluents by the solar photo-Fenton process in continuous flow at neutral pH in open reactors. Firstly, indoor assays were carried out with three hydraulic residence times (HRTs), 15, 30 and 60 min under simulated solar radiation of 30 W m^{-2}, 5 cm liquid depth, 20 mg Fe^{2+} L^{-1} and 50 mg H_2O_2 L^{-1}. At 60 and 30 min of HRT, wastewater disinfection below 1 CFU mL^{-1} was achieved at steady state for the three microbial groups selected. Nevertheless, at 15 min of HRT only 1-log inactivation was obtained. Taking into account the results obtained at laboratory scale, the best HRTs (60 and 30 min) were tested outdoors in 5 cm-deep RPRs in both summer and winter. The start-up began with a batch operation for 120 min with 20 mg Fe^{2+} L^{-1} and 50 mg H_2O_2 L^{-1}, followed by continuous operation over three consecutive days with 20 mg Fe^{2+} L^{-1} and 30 mg H_2O_2 L^{-1} to avoid large excess of hydrogen peroxide in steady state. Bacterial inactivation results showed 30 min of HRT to be the most efficient operation condition capable of producing 305 m^3 m^{-2} $year^{-1}$ of disinfected water while complying with the Spanish Law (RD 1620/2007) for water reuse. Additionally, a reduction in iron supply ranging from 10 to 2.5 mg L^{-1} in continuous mode with 30 mg H_2O_2 L^{-1} was evaluated. Efficient microorganism inactivation was reached for 10 and 5 mg Fe^{2+} L^{-1}, thus reducing the iron consumption at steady state four-fold. This research opens up a new line of research on the optimisation of wastewater disinfection by large-scale solar photo-Fenton.

1. Introduction

Over the last century, overall demand for water has grown, putting a strain on the available supplies. In this context, over the last few years the reuse of water has been put forward as an alternative option to help relieve the pressure on freshwater resources, especially in sectors such as agriculture, where water scarcity is critical [1]. Although in most of the EU countries suffering water scarcity (Italy, Greece, Cyprus, Spain and Portugal) the use of reclaimed water is an accepted practice for crop irrigation, there is not yet a common European guideline on water quality for wastewater reuse purposes. However, despite each member having developed its own water reuse standards, the minimum quality requirements for two water reuse applications: agricultural irrigation and aquifer recharge have recently been published with the aim of establishing a common level of health and environmental safety in all member states as well as providing the basis for defining EU legislation on water reuse [2].

As one of the main health and environmental risks related to water reuse in agricultural irrigation is the presence of pathogens (bacteria, viruses and protozoa), investigations have been directed towards wastewater reclamation technologies to guarantee proper disinfection. Chlorination is the most widely applied disinfection method [3,4], but the generation of toxic disinfection by-products has driven research towards alternative greener disinfection techniques such as Advanced Oxidation Processes (AOPs). Despite UV-radiation alone or in combination with H_2O_2 [5], or ozone being widely employed over the last few decades for inactivation of different microorganisms [5,6], the photo-Fenton process has emerged as an environmentally safe solution not only to remove chemical pollutants [7,8] but also for microbial inactivation [9].

In the Fenton reaction, iron acts as a catalyst and is constantly oxidized and reduced by hydrogen peroxide, generating hydroxyl

* Corresponding author at: Department of Chemical Engineering, University of Almería, 04120, Almería, Spain.
E-mail address: jsanchez@ual.es (J.A. Sánchez Pérez).

https://doi.org/10.1016/j.apcatb.2019.01.093
Received 26 September 2018; Received in revised form 26 December 2018; Accepted 31 January 2019
Available online 01 February 2019
0926-3373/

radicals responsible for nucleotides and amino acids breakdown of microorganisms. Moreover, in the presence of UV–vis radiation, the generation rate of $HO^{\cdot}$ is increased as the ferric ions are photo-reduced to ferrous iron [10,11].

Even though radical generation is favoured at acidic pH, several studies have proved the successful bacterial inactivation by the photo-Fenton process at neutral pH [12–14]. Nevertheless, further research on scaling up the process to large scale demo plants is still required. In this regard, one of the greatest challenges to achieve industrial applications of the photo-Fenton process is cost reduction, especially when related to both photoreactor investment and operating costs [15]. In fact, one approach to reduce these costs might be addressed by using low cost reactors such as raceway pond reactors (RPRs) instead of the most common system used for microorganism inactivation, the tubular reactor provided with compound parabolic collectors (CPC). Despite having less efficient optics than the latter, their low construction cost (around forty times lower than for the CPCs), along with the larger volume/surface ratio have brought RPRs as a very competitive option for scaling up this solar disinfection process of secondary effluents [16]. Similar disinfection times (80 min) have been observed in both reactors (CPC and 5 cm-deep RPR) with the most favourable conditions (20 mg Fe^{2+} L^{-1} and 50 mg H_2O_2 L^{-1}) being reported in a CPC pilot plant used to disinfect real wastewater by solar photo-Fenton at neutral pH [17].

Another key issue to achieve the large-scale photo-Fenton process implementation in RPRs is continuous operation, as batch operation might not be able enough to deal with the high volumes of secondary effluents released by a MWWTP. To date, while some research has been carried out on the continuous operation feasibility of solar photo-Fenton at acidic pH in RPR for micropollutant removal [18], no single study has been attempted that investigates the operational viability of the process in continuous flow for microorganism inactivation.

This work therefore set out to assess the operational viability for continuous flow operation of the solar photo-Fenton process at neutral pH for wastewater disinfection in 5 cm-deep RPRs at pilot plant scale. The effects of hydraulic residence time (HRT) and reactant dosage on pathogen bacteria inactivation were studied in steady state.

2. Materials and methods

2.1. Reagents

In order to carry out the photo-Fenton experiments ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$; > 99%) from Panreac (Spain) was used as iron source (Fe^{2+}) and hydrogen peroxide (33%, w/v aqueous solution) from Sigma-Aldrich (Spain) were used. Catalase, from Fluka (Spain) was used to remove the residual hydrogen peroxide present in the samples. Sulfuric acid (95–98%) acquired from Panreac (Spain), was used to prepare the iron stock solution for the continuous mode operation and ascorbic acid purchased form Sigma Aldrich (Spain) was used to reduce Fe^{3+} to Fe^{2+} for iron measurements with the o-phenantroline method.

2.2. Experimental set-up

Experiments were performed using secondary effluent from a municipal wastewater treatment plant (MWWTP) located near Almeria city (El Bobar, Spain). It is capacity is designed for a population equivalent of 100,000 and with an outlet flow of 11.6 hm^3 $year^{-1}$. Effluent samples were collected at the end of the secondary biological treatment in batches of 1000 L and used as received within 3 days. To avoid sedimentation of suspended solids in the store tank a gentle agitation was kept. All batches of water were characterized both on the day of reception and the following three days of experimentation. No significant changes in the main physic-chemical and microbiological parameters measured such as pH, turbidity, conductivity, COD, DOC, bicarbonates (measured as total inorganic carbon), anion concentration and bacterial concentrations were observed during the three days of experimentation in the stored effluent characteristics. Table S1 shows the average values and standard deviation of the main wastewater parameters used in the experimental period (from October 2017 to July 2018).

All tests were carried out at the Solar Energy Research Center (CIESOL), located at the University of Almeria (Spain) on sunny days. Irradiance was measured using the Avantes AvaSpec spectroradiometer, providing data in terms of incident UVA (W m^{-2}) in the wavelength range from 327 to 384 nm. The average values of solar UVA irradiance in winter within the period 12:00–17:00 local time in the three consecutive days of experimentation were 13.3 ± 4.7 W m^{-2} (HRT 30) and 14.7 ± 4.9 W m^{-2} (HRT 60), whereas for summer were 34.4 ± 2.5 W m^{-2} and 32.7 ± 2.4 W m^{-2} for HRT of 30 and 60 HRT, respectively. The average values of UVA were used to calculate the accumulated solar energy per unit volume (Q_{UVA}, kJ L^{-1}) during the continuous flow operation according to Eq. (1):

$$Q_{UVA} = \overline{UVA} \bullet \frac{A_r}{V_t} \bullet HRT \quad (1)$$

where $\overline{UVA}$ is the average of solar UVA, expressed in kW·m^{-2}, HRT is the Hydraulic Retention Time expressed in seconds, A_r is the illuminated area of the reactor (m^2) and V_t is the total volume of treated water (L).

Temperature (Crison 60 50) and pH (Crison 53 35) were monitored on-line by means of the U12 data acquisition device connected to a computer. The water temperature was around 22 °C in winter and 27 °C in summer. No significant changes were observed in the pH during all the experiments, remaining constant at 7.1 ± 0.2.

2.2.1. Laboratory scale experimentation under simulated solar light

A preliminary study was carried out at laboratory scale to assess the feasibility of continuous operation of Fenton and photo-Fenton processes for wastewater disinfection at neutral pH. To this end, the effect of three HRTs: 15, 30 and 60 min on pathogen inactivation was tested by monitoring wild Total Coliforms (TC), *Escherichia coli* (*E. coli*) and *Enterococcus sp*. as faecal contamination models. Experiments were performed in a 1 L-stirred cylindrical reactor made of polyvinyl chloride (PVC) whose characteristics were 5 cm liquid depth, 16 cm internal diameter and 2.4 s mixing time. The experimental runs were conducted under controlled conditions of irradiance in a solar simulator Sun Test CPS + set at 30 W m^{-2} and temperature at 25.0 °C (thermo Scientific NESLAB RTE-7 thermostatic bath). So as to check the possible disinfection not attributable to the photo-Fenton process, the continuous operation at each aforementioned HRT, was started initially in the absence of light with the supply of Fenton reagents and subsequently followed by the photo-Fenton process. The concentration of iron and hydrogen peroxide tested in both processes was 20 mg L^{-1} and 50 mg L^{-1}, respectively. Accordingly, once the reactor was filled with 1 L of secondary effluent it was covered and then the effluent and Fenton reagents were continuously added by the respective feed pumps at the required flow rates from the stock solutions to attain the selected HRT. After over 4 h of Fenton treatment in continuous flow, the reactor was uncovered and photocatalysis started.

2.2.2. Experimentation in outdoor RPR pilot plants

Solar photo-Fenton experiments for wastewater disinfection at neutral pH in continuous flow were carried out in outdoor conditions in two twin RPRs of 5 cm liquid depth. Experiments were carried out in duplicate. Reactors were made of PVC with a maximum working volume of 18 L and 3 min mixing time, whose dimensions were 0.98 m in length and 0.37 m in width. A scheme of the experimental set-up is shown in Fig. 1. Firstly, the effect of HRT on bacterial inactivation (TC, *E. coli* and *Enterococcus* sp.) was evaluated. Secondly, the reduction of iron concentration supply during the continuous flow was studied.

Outdoor experiments were carried out over three consecutive days

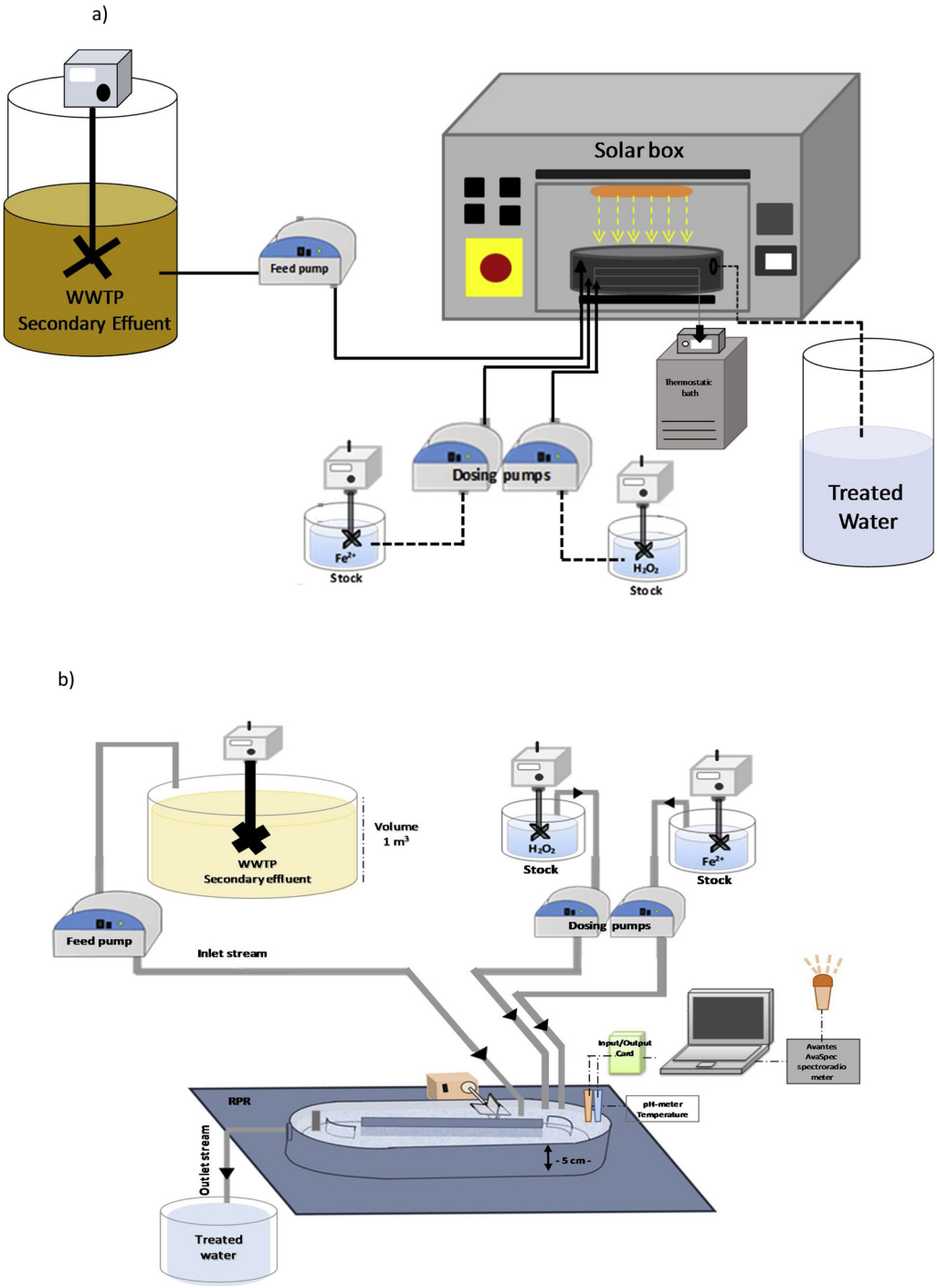


Fig. 1. Experimental setup for bacterial inactivation by solar photo-Fenton in continuous flow in (a) lab-scale and (b) outdoor conditions.

in winter and summer conditions from October 2017 to July 2018. On the first day, the solar photo-Fenton process was operated in batch mode for 2 h to reduce bacteria concentration. After that, the feed pumps of real secondary effluent, iron and hydrogen peroxide were switched on. Stock solutions were prepared for hydrogen peroxide and iron, this last one at pH 2.8 to avoid iron precipitation. The output stream was set by overflow and the continuous mode set in operation for 300 min. After this time, the reactors were kept loaded with the treated water overnight. For the next two consecutive days, the operation was run directly in continuous mode for 300 min.

To study the effect of HRT, iron concentration was set at 20 mg Fe^{2+} L^{-1} for both batch and continuous mode operation. The hydrogen peroxide concentration was 50 mg L^{-1} at the start of the batch operation according to [12,17] and the remaining H_2O_2 concentration was over 25 mg L^{-1} at the end of the batch. To avoid large excess of H_2O_2, its concentration in the inlet stream during the continuous mode was reduced to 30 mg L^{-1}. To study the effect of iron supply, the same operating conditions were assayed, except for the iron concentration in continuous mode which was reduced from 20 to 10, 5 and 2.5 mg Fe^{2+} L^{-1}.

2.3. Chemical and analytical determinations

Hydrogen peroxide concentration was determined with titanium

(IV) oxysulphate solution spectro-photometric method at 410 nm (method DIN 38 402 H15) with a Limit of Detection (LOD) of 0.3 mg L^{-1}.

Iron concentration was analyzed by the *o*-phenantroline standardized method according to ISO 6332 with a LOD of 0.5 mg L^{-1}. As in the presence of H_2O_2 most of the iron exists as ferric iron [19], ascorbic acid in excess was added to reduce all ferric iron to ferrous iron. At neutral pH most of the iron precipitates as iron hydroxides. Therefore, total iron (including soluble and insoluble forms), was measured in not filtered samples whereas to measure the dissolved iron, samples were filtered with 0.2 µm syringe-driven filters (Millex®, MILLIPORE). Dissolved organic carbon (DOC) and bicarbonate (as total inorganic carbon, TIC) determinations were carried out in a Shimadzu-VCPH TOC analyser, while anion concentrations were analyzed using ion chromatography (Metrohm 881 Compact IC pro) and the eluent used was a solution of 3.6 mM Na_2CO_3. Conductivity and turbidity measurements were made using a conductivity meter (PHYWE) and turbidity meter (HANNA), respectively. COD was measured with a commercial kit (Hanch LCK 314).

2.4. Bacterial quantification

The wild enteric bacteria concentrations (TC, *E. coli* and *Enterococcus sp.*) in the MWWTP effluent were evaluated using standard plate counting methods with serial dilutions in a Chromocult selective medium (Merck KGaA, Germany) for TC and *E. coli* and Enterococcus selective broth medium (Pronadisa, Madrid) for *Enterococcus* sp [20]. Colonies were counted after 24 h of incubation for TC and *E. coli*, and 48 h for *Enterococcus* sp. at 37 °C. The detection limit was 1 CFU mL^{-1}. All procedures were carried out in duplicate for each sample. The initial concentration range for the three microbiological groups selected (TC, *E. coli* and *Enterococcus* sp) was 10^5, 10^4 and 10^3 CFU mL^{-1}, respectively. In order to evaluate possible events of post-treatment bacterial reactivation, a re-growth study was carried out overnight with the treated effluent. To this end, 200 mL of treated water samples were stored with a hydrogen peroxide concentration of: 50, 40, 30, 15, 8 and 0 mg L^{-1}. The selected hydrogen peroxide concentrations were obtained by adding the required amount of the reagent to the residual concentration after photo-Fenton or by removing it with catalase [21]. Samples were kept in the dark at the outdoor temperature overnight. Following this, samples were incubated at 37 °C for one day for TC *and E. coli* colony counting and two days for *Enterococcus* sp.

2.5. Control experiments

Control experiments were carried out in the stirred tank reactor. These controls were as follows: i) in the absence of light without any reagent in order to verify the effect of mechanical stress under the established flow conditions. ii) With hydrogen peroxide and solar radiation (sunlight/H_2O_2), 50 mg L^{-1} being the concentration of hydrogen peroxide. Control experiments in RPR were reported elsewhere [17].

3. Results and discussion

3.1. Selection of hydraulic retention time at laboratory scale

The short disinfection times achieved with the solar photo-Fenton treatment of WWTP secondary effluents, between 60–120 min [12] to reach the detection limit of bacterial inactivation (1 CFU mL^{-1}), make it necessary to move from batch wise operation towards continuous flow operation. Nonetheless, as far as the authors know, there are no papers dealing with wastewater disinfection by solar processes in continuous flow. The first step was to assess the effect of HRT at laboratory scale. Three values of HRT were assayed, 60 min because it is the minimum required for batch wise operation, then halving this time twice (30 and 15 min) to seek out the inactivation capacity in continuous flow. First, the blank experiments were carried out to check the effects of mechanical stress and the synergic effect of UVA plus H_2O_2 in continuous flow at 60 min of HRT (Fig. S1). Mechanical stress only gave rise to a 1-log decrease in TC and no effect on *E. coli* and *Enterococcus sp*. Around a 1-log inactivation due to sunlight-H_2O_2 was observed with TC and *E. coli*. As for *Enterococcus* sp. its concentration remained unchanged regardless of the blank experimental condition assayed. The higher resistance shown by these Gram-positive enteric bacteria could be attributed to the presence of a more resistant cell wall as reported elsewhere [11]. Comparing these results with those previously reported during the batch operation in a tubular reactor provided with compound parabolic collectors [12], the mechanical stress had no effect on TC in the tubular reactor, and the combined action of sunlight and H_2O_2 led to approximately 1-log inactivation of TC after 60 min of treatment.

Continuous operation was started with Fenton reagent supply in the dark to take into account the disinfection by Fenton treatment as another blank experimental condition, along with bacterial removal due to iron hydroxide precipitation at neutral pH. The same effect was observed at the three values of HRT, around a 1-log decrease in TC concentration and no significant decrease in *E. coli* and *Enterococcus* once steady state was reached (Fig. 2).

The co-precipitation of bacteria and iron hydroxide particles can be disregarded because it is a physical phenomenon that is not dependent on bacterial species. As such, the slight decrease in Total Coliform concentration was attributed to mechanical stress according to the blanks. A quite different picture was observed when irradiation started. Regardless of the HRT, a 1-log decrease in Total Coliforms and *E. coli* concentrations took place, but not in *Enterococcus* sp. concentration when the reactor was illuminated, most likely due to the synergic effect of sunlight and H_2O_2 as shown in Fig. S1. Biologically, UVA radiation not only has a negative effect on bacterial DNA, but also on different cell compounds which play an important role in the metabolic cycle avoiding cell homeostasis. Key enzymes such as ribonucleotide, catalase and dihydroxy acid dehydratase that are involved in the elimination of H_2O_2 intracellular excess are inhibited by UVA radiation [22–24]. After that, a progressive bacterial inactivation occurred during the transition regime from dark steady state to illuminated steady state. This was due to the enhancement of the hydroxyl radical generation rate associated with the photo-Fenton reaction, and complete bacterial removal was attained at HRT of 30 and 60 min, pointing out the photocatalytic mechanism of cellular inactivation for the three species monitored [25]. Nonetheless, 15 min of hydraulic residence time was too short, and no more inactivation was attained after the initial drop caused by illumination in this operational condition.

Although there are many reactions and processes which work simultaneously during photo-Fenton treatment at neutral pH, the main mechanisms involved for bacterial inactivation are stated to be those related to (i) the generation of external hydroxyl radicals in Fenton and photo-Fenton reactions which attack the cellular membrane, ii) the damage generated due to the action of solar UVA and iii) the diffusion of iron and H_2O_2 into the cell (internal photo-Fenton reactions) [26]

Despite very little is found in the literature investigating the role of energy dose in pathogens inactivation during the solar photo-Fenton process at neutral pH, Ortega-Gómez et al. 2016 [27], demonstrated that microorganism's inactivation could be estimated as a linear function of the accumulated energy dose, Q_{UVA}. This variable takes into account the integrated irradiance which reaches the reactor surface along with the solar exposure time in terms of total energy received in the system per unit of volume (kJ L^{-1}) [28]. Q_{UVA} was calculated for the different hydraulic residence times through Eq. (1) giving 0.54, 1.08 and 2.16 kJ L^{-1} for 15, 30 and 60 min of HRT, respectively, at a constant irradiance of 30 W m^{-2}. As such, 15 min of HRT in both dark and illuminated conditions, gave similar inefficient microorganism inactivation as in the presence of light the solar exposure time was too short, limiting the energy received and therefore the amount of

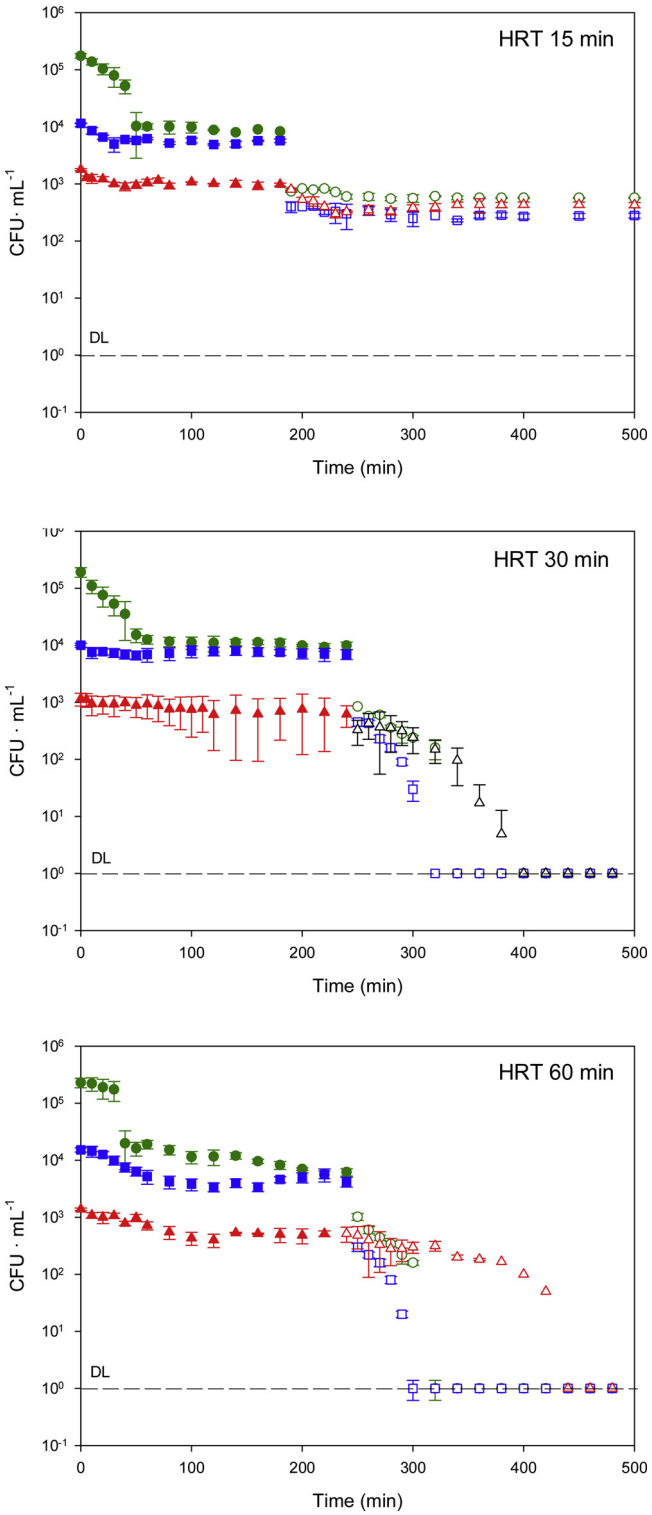


Fig. 2. Total coliforms (●), *E. coli* (■) and *Enterococcus* sp. (▲) inactivation by Fenton process (closed symbols) and photo-Fenton process with a radiation of 30 W m^{-2} (open symbols) in continuous mode (50 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}).

hydroxyl radicals generated. The low UVA dose (0.54 kJ L^{-1}) gave rise to low bacterial damage, as the process was photo-limited. However, longer solar exposure times of 30 and 60 min led to higher bacterial inactivation due to the higher energy and therefore hydroxyl radicals generated. From these results, at least 1 kJ L^{-1} is needed to inactivate bacteria under the LOD.

As for H_2O_2 consumption, the initial reaction between ferrous iron and H_2O_2 gave rise to an almost instantaneous consumption of 12 mg L^{-1}. Meanwhile the steady state concentrations decreased with HRT, with mean values of 22.0 ± 0.8 mg L^{-1}, 18.0 ± 1.2 mg L^{-1} and 15.0 ± 1.2 mg L^{-1} for 15 min, 30 min and 60 min HRT respectively, during the photo-Fenton treatment.

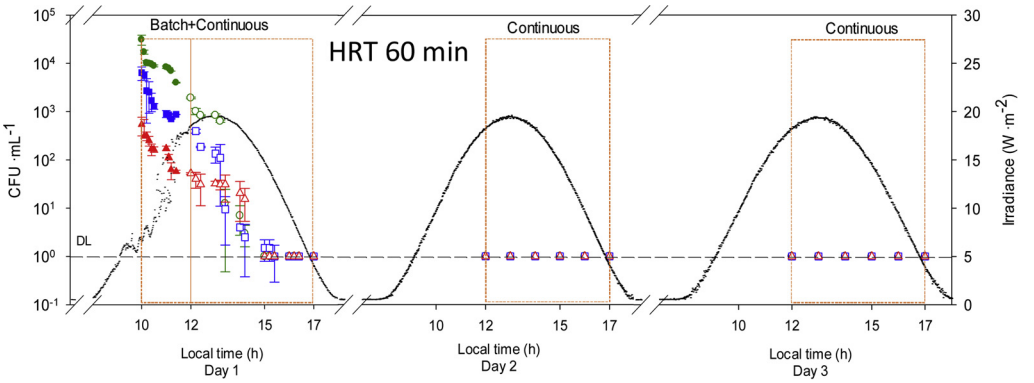
3.2. Outdoor raceway pond reactor operation for wastewater disinfection in continuous flow

Taking into account the results obtained at laboratory scale, the best HRTs (60 and 30 min) were tested outdoors in 5 cm deep RPRs. Only the experiments in which weather conditions led to microorganism inactivation below the detection limit (1 CFU mL^{-1}) are shown because no disinfection was achieved on cloudy days. Bearing in mind cost reduction, special attention was paid to reducing Fenton reactant consumption (hydrogen peroxide and ferrous iron). The hydrogen peroxide residual concentration is one of the most important factors at play to avoid the regrowth risk in the treated effluents as previously reported [29]. A regrowth assay was hence carried out during the first experimental set in order to determine the minimum concentration of H_2O_2 needed to avoid this post-treatment regrowth overnight as described in Section 2.3. This study showed that above 30 mg L^{-1} of H_2O_2 residual concentration, regrowth did not occur. However, below 15 mg L^{-1} of H_2O_2 residual concentration, regrowth was evident, showing increases of 3-log in TC and 2-log for *E. coli* and *Enterococcus sp*. This is why 30 mg L^{-1} of H_2O_2 was selected as the minimum hydrogen peroxide concentration required overnight to avoid bacterial regrowth.

Results obtained during winter are shown in Fig. 3. Bacterial inactivation below 1 CFU mL^{-1} was not achieved during the 2 h of batch operation mode. This was due to the low solar UVA irradiance levels reached in winter, all of them below 20 W m^{-2} since the temperature remained around 22 °C. This is an important factor due to the strong influence of UVA irradiation and temperature on the wastewater disinfection process as shown in recent studies [27,30]

However, significant differences can be observed between the two HRTs tested working in continuous mode. In the case of 30 min of HRT, the system was not able to achieve bacterial concentration below the requirement by Spanish legislation (1 CFU *E. coli* mL^{-1}) whilst for 60 min of HRT the disinfection below 1 CFU mL^{-1} was produced during continuous mode in the first day. These differences could be due to the bacterial inactivation rate for each HRT tested. The longer exposure time achieved at 60 HRT causes higher cell damage due to $HO^{\cdot}$ attack and consequently higher values for the bacterial inactivation rate than flow input rate. Therefore, the system achieved steady state below 1 CFU·mL^{-1}. However, the exposure time achieved in the case of 30 min of HRT was not long enough and a steady state was reached at the bacterial concentration for which the specific bacterial inactivation rate and the dilution rate were equal. These differences in bacterial inactivation can be explained in terms of energy dose. The calculated Q_{UVA} were 0.48 and 1.06 kJ L^{-1} for HRT of 30 and 60 min, respectively. As expected, no significant bacteria inactivation was reached with 30 min of HRT under average irradiance of 13.3 ± 4.7 W m^{-2} since 0.48 kJ L^{-1} was below that obtained in indoor conditions (0.54 kJ L^{-1}) under constant irradiance of 30 W m^{-2} and 15 min of HRT, confirming the results obtained with the solar light simulator. On the contrary, with longer solar exposure times as obtained with HRT of 60 min and an average irradiance of 14.7 ± 4.9 W m^{-2} reaching a value of Q_{UVA} of 1.06 kJ L^{-1}, higher amounts of $HO^{\cdot}$ were generated leading to achieve disinfection below 1 CFU mL^{-1} as equally obtained in indoor conditions with a Q_{UVA} value of 1.08 kJ L^{-1} (HRT 30 min, 30 W m^{-2}).

Once the continuous treatment was finished on the first day, the reactor was kept loaded with the treated water overnight. The residual hydrogen peroxide concentration in the reactor after 300 min of continuous treatment was 22.0 ± 0.8 mg L^{-1} in the case of 30 min of HRT and 18.0 ± 0.7 mg L^{-1} for 60 min. remaining around these values on



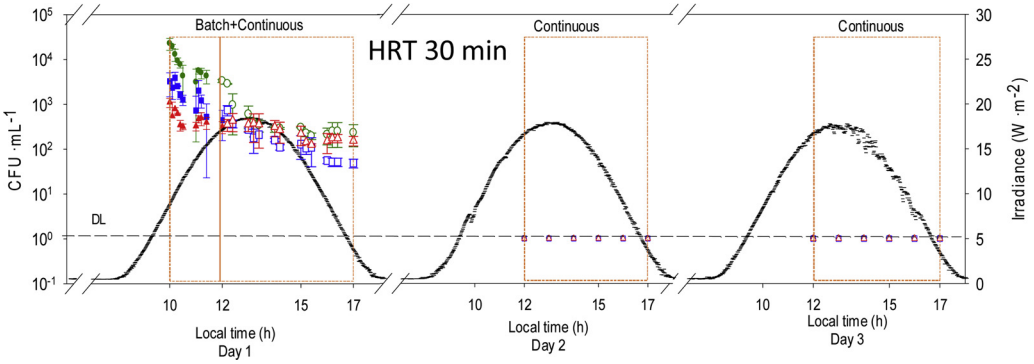
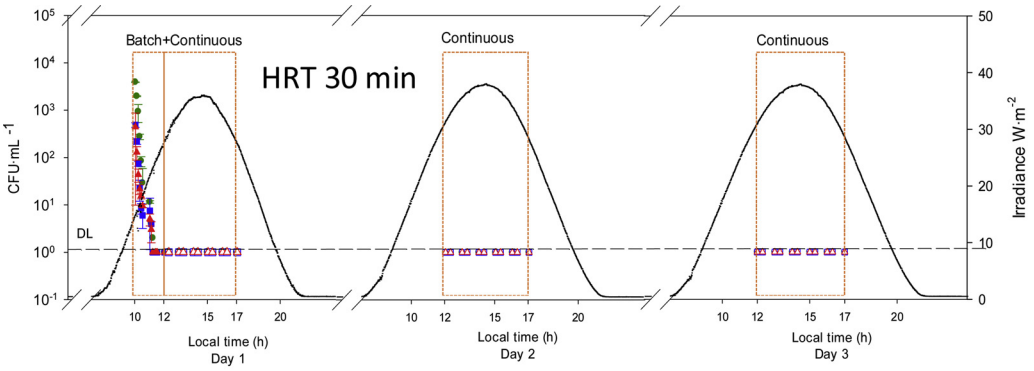


Fig. 3. Total coliforms (●), *E. coli* (■) and *Enterococcus* sp. (▲) inactivation by photo-Fenton process in batch (closed symbols; 50 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}) and continuous flow (open symbols; 30 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}) under winter conditions at different HRTs.



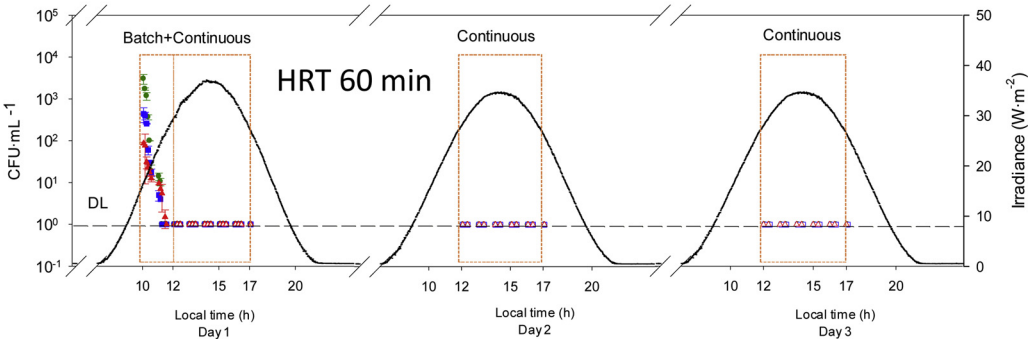


Fig. 4. Total coliforms (●), *E. coli* (■) and *Enterococcus* sp. (▲) inactivation by photo-Fenton process in batch (closed symbols; 50 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}) and continuous flow (open symbols; 30 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}) under summer conditions at different HRTs.

the second and third experimental days. At this point, bacteria were highly damaged, being seen to be in an injured state. As mentioned in a previous study [29], bacteria are able to regrow. Consequently, to avoid regrowth risks overnight, up to 30 mg L^{-1} of hydrogen peroxide was added in both cases.

The next day bacterial inactivation below 1 CFU mL^{-1} was found for all the species studied, just before the resetting the continuous flow operation. As pointed out by other authors [29], the combined effect of Fenton during the night and photo-Fenton processes when there is light before the continuous operation started, might explain the complete inactivation achieved during the 30 min of HRT and regrowth inhibition during 60 min of HRT at the beginning of the next experimental day. Thus, Fenton overnight plus photo-Fenton effect caused serious damage to the bacteria, which implies that for both HRTs during continuous mode operation, the inactivation rate was higher than the input flow giving rise the bacterial inactivation below 1 CFU mL^{-1} [31].

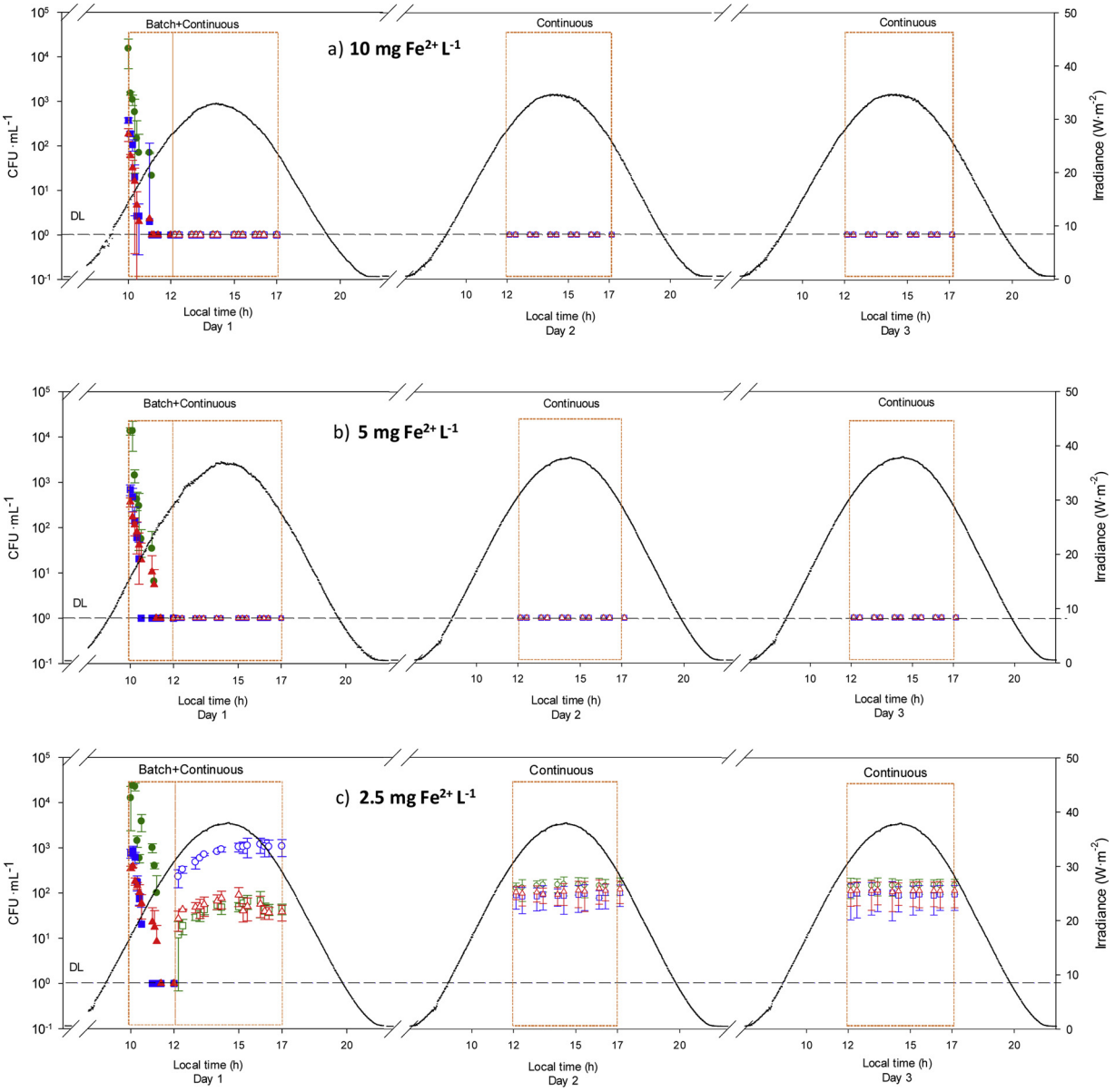


Fig. 5. Total coliforms (●), *E. coli* (■) and *Enterococcus* sp. (▲) inactivation by photo-Fenton process in batch (closed symbols; 50 mg H_2O_2 L^{-1}- 20 mg Fe^{2+} L^{-1}) and continuous flow (open symbols), 30 mg H_2O_2 L^{-1} – (a) 10 mg Fe^{2+} L^{-1} (b) 5 mg Fe^{2+} L^{-1} and (c) 2,5 mg Fe^{2+} L^{-1}, under summer conditions at 30 min of HRT.

Once the second experimental day ended, sufficient hydrogen peroxide (until 30 mg L^{-1}) was added once again to diminish the regrowth risk overnight. On the third experimental day, no bacterial regrowth was observed overnight and the bacterial inactivation below 1 CFU·mL^{-1} was maintained during the treatment time. At both HRTs, bacterial inactivation below the detection limit was achieved for the three microbiological groups selected.

Results obtained in summer at 30 and 60 min of HRT are showcased in Fig. 4. Bacterial inactivation below 1 CFU·mL^{-1} was achieved in the 2 h-batch operation, mainly due to the higher irradiance (below 40 W m^{-2}) and temperature (around 27 °C). As reported in a previous study, the higher the radiation intensity, the higher the hydroxyl radical production, thus increasing bacterial inactivation rate [27]. Additionally, the higher the temperature, the higher the bacterial inactivation rate [30]. The inactivation times during the batch mode operation (around 80 min) were in line with those reported by Esteban et al., in summer in RPRs [17]. This demonstrates the high efficiency and reproducibility of the treatment. Bacterial inactivation below 1 CFU mL^{-1} was kept for both HRTs during the steady state and maintained for the second and third experimental day, pointing out the robustness of the treatment.

In this case bacterial inactivation was not limited by the solar energy received in the system in concordance with our earlier observations indoors, because of Q_{UVA} values were 1.24 kJ L^{-1} for 30 min of HRT (34.4 ± 2.4 W m^{-2}) and 2.35 kJ L^{-1} for 60 min of HRT (32.7 ± 2.4 W m^{-2}).

The residual H_2O_2 in this case was 13 mg L^{-1} for 30 min and 8 mg L^{-1} for 60 min of HRT. As described above, after each operation in continuous mode, a certain amount of hydrogen peroxide (until 30 mg L^{-1}) was added to avoid regrowth risk overnight.

In summary, to comply with the Spanish legislation for water reuse, after the batch phase the continuous one should start off at 60 min of HRT the first day, subsequently being reduced to 30 min the second and following operation days in winter. In summer, 30 min of HRT can be set from the first day of continuous operation. It is interesting to remark that if the reuse of the treated water takes place immediately after treatment, no further H_2O_2 is necessary and the residual H_2O_2 is suitable for crop irrigation in greenhouses [32]. In contrast, if the goal is to

store the treated water, a high enough amount of hydrogen peroxide should be added in order to avoid the regrowth risk for the following days.

3.3. Effect of iron concentration during continuous flow operation

Once the feasibility of the continuous flow operation had been demonstrated, the next step in the experimental schedule was the reduction in iron supply. The iron concentration plays an important role in the disinfection process because it acts as catalyst of the heterogeneous photo-Fenton process at neutral pH as previously reported [33].

To this end, the same RPR of 5 cm liquid depth was operated at 30 min of HRT. The reactor start-up was carried out as described above and after that the continuous supply of reactants was set at 30 mg H_2O_2 L^{-1} and iron concentration in the inlet stream was reduced to 10, 5 and 2.5 mg Fe^{2+} L^{-1} for different runs (Fig. 5).

In the case of 10 and 5 mg Fe^{2+} L^{-1}, similar disinfection behavior can be observed. Both iron concentrations tested were able to maintain the steady state below the concentration limit required by Spanish legislation with substantial reactant saving. Although at neutral pH most of the iron added precipitates as iron hydroxides, it is active in the generation of $HO^{\cdot}$ in the heterogeneous photo-Fenton process [33] (in all cases studied, the remaining dissolved iron concentration measured was below the LOD). Altogether, apart from the aforementioned external hydroxyl radical generation, the internal $HO^{\cdot}$ production via internal Fenton reactions promoted by iron diffusion into the cells, are considered as the main mechanisms responsible for bacterial inactivation [34,35] Reactive oxygen species are able to produce detrimental effects on cells, not only affecting the external membrane structure but also by damaging DNA molecules or disrupting vital internal metabolic activities [35].

As such, as can be observed in Fig. 5a and b, both the external and internal $HO^{\cdot}$ generated in continuous flow with 5 and 10 mg L^{-1} were able to keep the steady state under the detection limit. In these cases, total iron concentration once steady state was reached, remained at 6 and 12 mg L^{-1} for both cases. These concentrations were slightly higher due to the deposition of part of the precipitates at the bottom of the reactor. However, with a lower iron concentration (2.5 mg Fe^{2+} L^{-1}) the $HO^{\cdot}$ production rate in the continuous mode was not able to efficiently inactivate bacteria (Fig. 5c) and consequently the bacterial concentration increased up to a constant concentration in the steady state around 10^2 CFU mL^{-1} for the three microbiological groups selected. In this operating condition, 3 mg L^{-1} was the total iron concentration during the steady state.

As for the treatment capacity, taking into account the amount of sun hours available per year above a minimum UVA irradiance of 10 W m^{-2}, which was reported to be 3055 h in Almería, Spain (latitude 36° 49′ N, longitude 2°24′W) [36], a 5 cm deep-RPR operated in continuous flow mode at 30 min of HRT can yield 305 m^3 m^{-2} $year^{-1}$. This is three times higher than that calculated for discontinuous operation in the same reactor with batches of 90 min [17], 114 m^3 m^{-2} $year^{-1}$.

4. Conclusions

The present study shows, for the first time, the feasibility of the disinfection of WWTP secondary effluents at neutral pH by solar photo-Fenton in RPRs working in continuous flow for all seasons of the year. A 5 cm deep-RPR operated at 30 min of HRT with 30 mg L^{-1} of H_2O_2 and 5 mg L^{-1} of Fe can produce 305 m^3 m^{-2} $year^{-1}$ of disinfected water. The water treated fulfilled the microbiological quality requirement for wastewater reuse in irrigation as per Spanish legislation. Additionally, bacterial regrowth was avoided using a concentration of 30 mg L^{-1} H_2O_2 in the treated water storage tank. The findings reported in this study have shed new light on the future implementation at large scale of the solar photo-Fenton process for wastewater disinfection in open reactors and lay the groundwork for future research into the optimization of the process in continuous mode.

Acknowledgments

This Special Issue is dedicated to honor the retirement of Prof. César Pulgarin at the Swiss Federal Institute of Technology (EPFL, Switzerland), a key figure in the area of Catalytic Advanced Oxidation Processes. This research was supported by the Ministry of Economy and Competitiveness (Government of Spain) project CTQ2016-78255-R, the Andalusian Regional Government (P12-RNM-1437) and the European Regional Development Fund (ERDF). I. de la Obra would like to acknowledge the Andalusian Regional Government for her grant.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.01.093.

References

[1] P. Drechsel, A. Bahri, L. Raschid-Sally, M. Redwood (Eds.), Wastewater Irrigation and Health, Routledge, USA, 2009, , https://doi.org/10.4324/9781849774666.
[2] L. Alcalde-Sanz, B. Gawlik, Minimum Quality Requirements for Water Reuse in Agricultural Irrigation and Aquifer Recharge: Towards a Legal Instrument on Water Reuse, (2017), https://doi.org/10.2760/887727.
[3] S. Casani, M. Rouhany, S. Knøchel, A discussion paper on challenges and limitations to water reuse and hygiene in the food industry, Water Res. 39 (2005) 1134–1146, https://doi.org/10.1016/j.watres.2004.12.015.
[4] S.-S. Liu, H.-M. Qu, D. Yang, H. Hu, W.-L. Liu, Z.-G. Qiu, A.-M. Hou, J. Guo, J.-W. Li, Z.-Q. Shen, M. Jin, Chlorine disinfection increases both intracellular and extracellular antibiotic resistance genes in a full-scale wastewater treatment plant, Water Res. 136 (2018) 131–136, https://doi.org/10.1016/j.watres.2018.02.036.
[5] J. Rodriguez-Chueca, M.P. Ormad, R. Mosteo, J. Sarasa, J.L. Ovelleiro, Conventional and advanced oxidation processes used in disinfection of treated Urban wastewater, Water Environ. Res. 87 (2015) 281–288, https://doi.org/10.2175/106143014X13987223590362.
[6] J.E. Drinan, Sources, intake, and screening, Water Wastewater Treat, CRC Press, 2012, pp. 75–88, https://doi.org/10.1201/b12354-7.
[7] G. Rivas Ibáñez, M. Bittner, Z. Toušová, M.C. Campos-Mañas, A. Agüera, J.L. Casas López, J.A. Sánchez Pérez, K. Hilscherová, Does micropollutant removal by solar photo-Fenton reduce ecotoxicity in municipal wastewater? A comprehensive study at pilot scale open reactors, J. Chem. Technol. Biotechnol. 92 (2017) 2114–2122, https://doi.org/10.1002/jctb.5212.
[8] I. De la Obra, L. Ponce-Robles, S. Miralles-Cuevas, I. Oller, S. Malato, J. Sánchez Pérez, Microcontaminant removal in secondary effluents by solar photo-Fenton at circumneutral pH in raceway pond reactors, Catal. Today 287 (2017) 10–14, https://doi.org/10.1016/J.CATTOD.2016.12.028.
[9] N. Klamerth, S. Malato, A. Agüera, A. Fernández-Alba, Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: a comparison, Water Res. 47 (2013) 833–840, https://doi.org/10.1016/j.watres.2012.11.008.
[10] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84, https://doi.org/10.1080/10643380500326564.
[11] S. Giannakis, M.I. Polo-López, D. Spuhler, J.A. Sánchez-Pérez, P. Fernández-Ibáñez, C. Pulgarin, Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction—part 2: a review of the applications for drinking water and wastewater disinfection, Appl. Catal. B Environ. 198 (2016) 431–446, https://doi.org/10.1016/j.apcatb.2016.06.007.
[12] E. Ortega-Gómez, B. Esteban, M.M. Ballesteros Martín, P. Fernández Ibáñez, J.A. Sánchez Pérez, Inactivation of natural enteric bacteria in real municipal wastewater by solar photo-Fenton at neutral pH, Water Res. 63 (2014) 316–324, https://doi.org/10.1016/j.watres.2014.05.034.
[13] L. Ioannou-Ttofa, S. Raj, H. Prakash, D. Fatta-Kassinos, Solar photo-Fenton oxidation for the removal of ampicillin, total cultivable and resistant E. coli and ecotoxicity from secondary-treated wastewater effluents, Chem. Eng. J. 355 (2019) 91–102, https://doi.org/10.1016/J.CEJ.2018.08.057.
[14] P. Villegas-Guzman, S. Giannakis, R.A. Torres-Palma, C. Pulgarin, Remarkable enhancement of bacterial inactivation in wastewater through promotion of solar photo-Fenton at near-neutral pH by natural organic acids, Appl. Catal. B Environ. 205 (2017) 219–227, https://doi.org/10.1016/j.apcatb.2016.12.021.
[15] J.A. Sánchez Pérez, I.M. Román Sánchez, I. Carra, A. Cabrera Reina, J.L. Casas López, S. Malato, Economic evaluation of a combined photo-Fenton/MBR process using pesticides as model pollutant. Factors affecting costs, J. Hazard. Mater. 244 (2013) 195–203, https://doi.org/10.1016/j.jhazmat.2012.11.015.
[16] I. Carra, L. Santos-Juanes, F.G. Acién Fernández, S. Malato, J.A. Sánchez Pérez, New approach to solar photo-Fenton operation. Raceway ponds as tertiary treatment

technology, J. Hazard. Mater. 279 (2014) 322–329, https://doi.org/10.1016/j.jhazmat.2014.07.010.
[17] B. Esteban García, G. Rivas, S. Arzate, J.A. Sánchez Pérez, Wild bacteria inactivation in WWTP secondary effluents by solar photo-fenton at neutral pH in raceway pond reactors, Catal. Today. 313 (2018) 72–78, https://doi.org/10.1016/j.cattod.2017.10.031.
[18] S. Arzate, J.L. Garcia Sánchez, P. Soriano-Molina, J.L. Casas Lopez, M.C. Campos-Mañas, A. Aguera, J.A. Sanchez, Perez, Effect of residence time on micropollutant removal in WWTP secondary effluents by continuous solar photo-Fenton process in raceway pond reactors, Chem. Eng. J. 316 (2017) 1114–1121, https://doi.org/10.1016/j.cej.2017.01.089.
[19] A. Cabrera Reina, L. Santos-Juanes, J.L. García Sánchez, J.L. Casas López, M.I. Maldonado, G. Li Puma, J.A. Sánchez Pérez, Modelling the photo-Fenton oxidation of the pharmaceutical paracetamol in water including the effect of photon absorption (VRPA), Appl. Catal. B Environ. 166–167 (2015) 295–301, https://doi.org/10.1016/j.apcatb.2014.11.023.
[20] E. Ortega-Gómez, B. Esteban García, M.M. Ballesteros Martín, P. Fernández Ibáñez, J.A. Sánchez Pérez, Inactivation of Enterococcus faecalis in simulated wastewater treatment plant effluent by solar photo-Fenton at initial neutral pH, Catal. Today. 209 (2013) 195–200, https://doi.org/10.1016/j.cattod.2013.03.001.
[21] A.M. Freitas, G. Rivas, M.C. Campos-Mañas, J.L. Casas López, A. Agüera, J.A. Sánchez Pérez, Ecotoxicity evaluation of a WWTP effluent treated by solar photo-Fenton at neutral pH in a raceway pond reactor, Environ. Sci. Pollut. Res. 24 (2017) 1093–1104, https://doi.org/10.1007/s11356-016-7101-7.
[22] A. Eisenstark, Bacterial gene products in response to near-ultraviolet radiation, Mutat. Res. Mol. Mech. Mutagen. 422 (1998) 85–95, https://doi.org/10.1016/S0027-5107(98)00178-X.
[23] P. Chelikani, I. Fita, P.C. Loewen, Diversity of structures and properties among catalases, Cell. Mol. Life Sci. 61 (2004) 192–208, https://doi.org/10.1007/s00018-003-3206-5.
[24] E. Smyk-Randall, O.R. Brown, A. Wilke, A. Eisenstark, D.H. Flint, Near ultraviolet light inactivation of dihydroxyacid dehydratase in Escherichia coli, Free Radic. Biol. Med. 14 (1993) 609–613, https://doi.org/10.1016/0891-5849(93)90142-H.
[25] S. Giannakis, M.I. Polo López, D. Spuhler, J.A. Sánchez Pérez, P. Fernández Ibáñez, C. Pulgarin, Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction—part 1: a review of the mechanisms and the fundamental aspects of the process, Appl. Catal. B Environ. 199 (2016) 199–223, https://doi.org/10.1016/J.APCATB.2016.06.009.
[26] I. García-Fernández, S. Miralles-Cuevas, I. Oller, S. Malato, P. Fernández-Ibáñez, M.I. Polo-López, Inactivation of E. coli and E. faecalis by solar photo-Fenton with EDDS complex at neutral pH in municipal wastewater effluents, J. Hazard. Mater. (2018), https://doi.org/10.1016/J.JHAZMAT.2018.07.037.
[27] E. Ortega-Gómez, M.M.B. Martín, B.E. García, J.A.S. Pérez, P.F. Ibáñez, Wastewater disinfection by neutral pH photo-Fenton: the role of solar radiation intensity, Appl. Catal. B Environ. 181 (2016) 1–6, https://doi.org/10.1016/J.APCATB.2015.06.059.
[28] S. Malato, P. Fernández-Ibáñez, M.I. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, Catal. Today. 147 (2009) 1–59, https://doi.org/10.1016/J.CATTOD.2009.06.018.
[29] S. Giannakis, M. Voumard, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Micropollutant degradation, bacterial inactivation and regrowth risk in wastewater effluents: influence of the secondary (pre)treatment on the efficiency of advanced oxidation processes, Water Res. 102 (2016) 505–515, https://doi.org/10.1016/J.WATRES.2016.06.066.
[30] E. Ortega-Gómez, P. Fernández-Ibáñez, M.M. Ballesteros Martín, M.I. Polo-López, B. Esteban García, J.A. Sánchez Pérez, Water disinfection using photo-Fenton: effect of temperature on Enterococcus faecalis survival, Water Res. 46 (2012) 6154–6162, https://doi.org/10.1016/J.WATRES.2012.09.007.
[31] R.D. 1620/2007, 7 de diciembre, por el que se establece el régimen jurídico de la reutilización de las aguas depuradas. 2019 BOE no294, (n.d.) (2007) http:/www.boe.es/boe/dias/2003/02//21/pdfs/A07228-.
[32] C. Sichel, P. Fernández-Ibáñez, M. de Cara, J. Tello, Lethal synergy of solar UV-radiation and H2O2 on wild Fusarium solani spores in distilled and natural well water, Water Res. 43 (2009) 1841–1850, https://doi.org/10.1016/J.WATRES.2009.01.017.
[33] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, M. Bensimon, J. Vélez-Colmenares, N. Benítez, C. Pulgarín, Iron oxides semiconductors are efficients for solar water disinfection: a comparison with photo-Fenton processes at neutral pH, Appl. Catal. B Environ. 166–167 (2015) 497–508, https://doi.org/10.1016/J.APCATB.2014.12.007.
[34] M.I. Polo-López, M. Castro-Alférez, I. Oller, P. Fernández-Ibáñez, Assessment of solar photo-Fenton, photocatalysis, and H2O2 for removal of phytopathogen fungi spores in synthetic and real effluents of urban wastewater, Chem. Eng. J. 257 (2014) 122–130, https://doi.org/10.1016/j.cej.2014.07.016.
[35] S. Giannakis, C. Ruales-Lonfat, S. Rtimi, S. Thabet, P. Cotton, C. Pulgarin, Castles fall from inside: evidence for dominant internal photo-catalytic mechanisms during treatment of Saccharomyces cerevisiae by photo-Fenton at near-neutral pH, Appl. Catal. B Environ. 185 (2016) 150–162, https://doi.org/10.1016/J.APCATB.2015.12.016.
[36] A. Cabrera Reina, J.L. Casas López, M.I. Maldonado Rubio, L. Santos-Juanes Jordá, J.L. García Sánchez, J.A. Sánchez Pérez, Effects of environmental variables on the photo-Fenton plant design, Chem. Eng. J. 237 (2014) 469–477, https://doi.org/10.1016/J.CEJ.2013.10.046.